ACS Macro Letters

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Colloidal Random Terpolymers: Controlling Reactivity Ratios of Colloidal Comonomers via Metal Tipping

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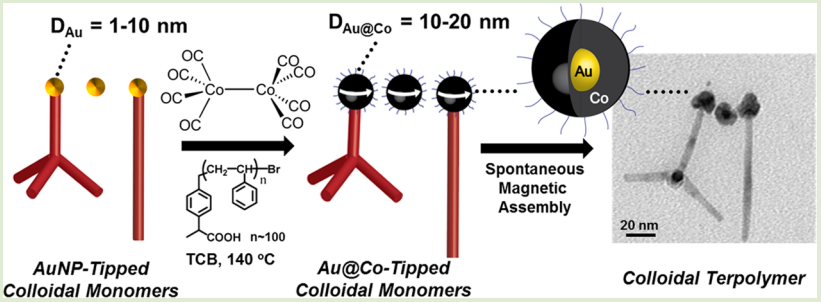
Supporting Information



ABSTRACT: We report on a versatile synthetic method of preparing colloidal copolymers and terpolymers composed of dipolar Au@Co core−shell nanoparticles (NPs) in the backbone, along with semiconductor CdSe@CdS nanorod (NR), or tetrapod (TP) side chain groups. A seven-step colloidal total synthesis enabled the synthesis of well-defined colloidal comonomers composed of a dipolar Au@CoNP attached to a single CdSe@CdS NR, or TP, where magnetic dipolar associations between Au@CoNP units promoted the formation of colloidal co- or terpolymers. The key step in this synthesis was the ability to photodeposit a single AuNP tip onto CdSe@CdS NR or TP that enables selective seeding of a dipolar CoNP onto the AuNP seed. We show that the variation of the AuNP size directly controlled the size and dipolar character of the CoNP tip, where the size modulation of the Au and Au@CoNP tips is analogous to control of comonomer reactivity ratios in classical copolymerization processes.

The use of well-defined inorganic nanoparticles as monomeric units to form one-dimensional (1-D) assemblies, termed "colloidal polymers", has recently gained attention as a route to prepare nanocomposites that possess intriguing optical, catalytic, and electrochemical properties.[1−4] Current efforts in this field have focused on the synthesis of new colloidal monomers that possess strong associative and directional noncovalent interactions, which promote selective 1-D polymerizations as opposed to poorly defined network aggregation.[5−11] To this end, recent advances in the total synthesis of complex inorganic colloids, coupled with selective methods to promote "colloidal polymerization", have enabled a wide variety of colloidal polymers to be prepared. These polymers are formed by harnessing noncovalent secondary interactions designed into the monomers, such as nanoparticle (NP) surface associations, electrostatic forces, or dipolar associations. The focus of our work and this report has been the preparation of colloidal monomers incorporating ferromagnetic metallic cobalt nanoparticles (CoNPs) which spontaneously form 1-D colloidal polymers via dipole interactions between CoNP units. Furthermore, we have also shown that noble metal colloidal NPs, such as gold (AuNPs),[6,10] can serve as seeds to promote selective deposition and overcoating of a ferromagnetic CoNP shell to form dipolar Au@CoNP colloidal monomers that spontaneously polymerize to form dipolar colloidal polymers (Figure 1a).

A major motivation in the field of colloidal polymers has been the application of classical polymer science concepts to these systems, such as, the control of macromolecular degree of polymerization, architecture, and composition. To this end, Kumacheva et al. reported on the preparation of Au nanorods (AuNR) with lateral hydrophilic CTAB ligands and hydrophobic polystyrene functionalized termini which, upon exposure to THF:water solutions, were observed to form linear polymers via tip-to-tip interactions.[12] Furthermore, the degree of polymerization was shown to be tunable as a function of reaction time.[3] Kotov et al. demonstrated the ability to control colloidal copolymer compositions by the formation of alternating copolymers of differently sized AuNPs achieved via polymerase chain reactions (PCR) from the surface of the AuNPs.[13] Additionally, segmented copolymers have been recently reported by Chen et al. via the pH-dependent copolymerization of AuNPs functionalized with poly(styrene-

Received: July 4, 2016
Accepted: July 21, 2016
Published: July 26, 2016

DOI: 10.1021/acsmacrolett.6b00511
ACS Macro Lett. 2016, 5, 950−954

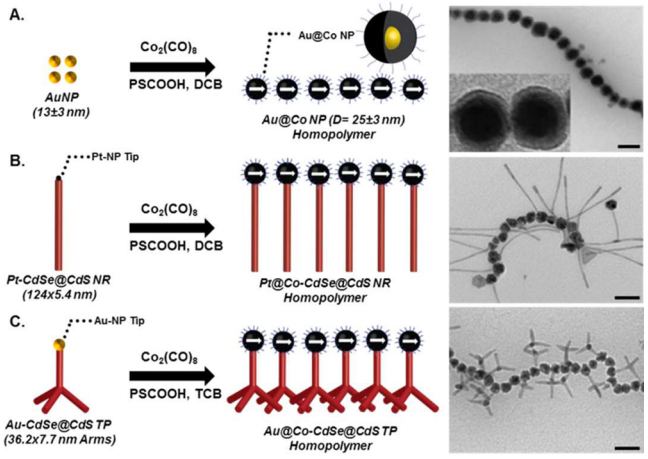


Figure 1. Colloidal homopolymers based upon dipolar cobalt nanoparticle association. (a) Au@Co dipolar colloidal polymers, synthesized by deposition of cobalt onto preformed metal (Au) NP seeds. Reprinted (adapted) with permission from *Chem. Commun.* **2011**, *47*, 890−892. RSC Copyright 2010. (b) Dipolar "bottlebrush" homopolymers bearing CdSe@CdS NR pendant groups, synthesized by deposition of cobalt onto the metal (Pt) NP portion of preformed Pt-CdSe@CdS NR. Reprinted (adapted) with permission from *ACS Nano* **2014**, *8* (4), pp 3272−3284. ACS Copyright 2014. (c) Dipolar homopolymers with "giant *t*-butyl" groups, synthesized by deposition of cobalt onto the preformed metal (Au) NP portion of preformed Au-CdSe@CdS TPs. Reprinted (adapted) with permission from *Angew. Chem., Int. Ed.* **2015**, *55* (5), 1787−1791. Wiley Copyright 2015. All scale bars are 50 nm.

block-poly(acrylic acid)) (PS-*b*-PAA) ligand shells.[14] The preparation of colloidal statistical copolymers has also been recently demonstrated.[10,11,14]

Our group has demonstrated the preparation of colloidal polymers of bare core−shell NPs (Au@CoNPs) that associate via north−south (N−S) dipolar interactions to form robust 1-D assemblies (Figure 1a).[6,15] We have also demonstrated the ability to prepare more complex dipolar colloidal monomers by combining dipolar CoNPs with CdSe@CdS nanorods.[16]

The key synthetic breakthrough to prepare these heterostructured colloidal monomers was the selective deposition of a single dipolar CoNP tip onto a noble metal (e.g., Au, Pt) NP tipped CdSe@CdS nanorod, where the Au, or PtNP tipped CdSe@CdS NR were synthesized using the methods of Banin et al.[17] The presence of a single dipolar CoNP tip onto the CdSe@CdS NP resulted in spontaneous NP polymerization to form colloidal bottlebrush polymers, wherein each monomer unit was composed of a Pt@Co dipolar nanoparticle bearing a pendant nanorod group (Figure 1b). Similarly, we have extended this methodology to CdSe@CdS tetrapods that carry a single dipolar NP tip that form colloidal polymers that carry tetrapods as side chain groups resembling "giant *t*-butyl groups" (Figure 1c) .[18] To prepare these dipolar tetrapods, the deposition of a single dipolar CoNP tip was conducted onto a CdSe@CdS tetrapod that contained a single AuNP tip. For each of these dipolar colloidal polymer systems, statistical copolymers have also been accessed where Pt-tipped NRs of varying length (see Supporting Information, Figure S10a) or Au-tipped TPs with free AuNP (see Supporting Information, Figure S10b) are isotropically blended in solution prior to cobalt deposition, resulting in statistical copolymers. While these earlier reports demonstrate the ability to prepare dipolar colloidal copolymers of varying composition, there remains a need to develop methods to enable copolymerization of colloidal monomers with disparate NP side chains as well as the ability to controllably tune copolymer composition.

Herein, we report on the controllable synthesis of colloidal statistical and segmented copolymers incorporating CdSe@CdS NRs, CdSe@CdS TPs, and bare AuNP units. We demonstrate for the first time that the controllable photodeposition of a single AuNP tip onto both CdSe@Cd NRs and TPs enables deposition of a single dipolar CoNP shell which spontaneously assembles into colloidal random copolymers. Furthermore, we show for the first time that the composition of these co- or terpolymers can be directly controlled by the size of AuNP tips (and subsequently the CoNP shell) on the NRs and TPs to ultimately prepare either random or block-like colloidal copolymers. The ability to control the copolymerization kinetics of these dipolar colloidal monomers by AuNP tip size has previously been unexplored and is analogous to the concept of comonomer reactivity ratios as observed in classical polymer chemistry.[19,20] An attractive feature of this system is the ability to directly image copolymer composition using TEM.

The general strategy for this work initially required the selective deposition of a single Au@CoNP tip onto CdSe@CdS NRs and TPs. As alluded to previously, in this seven-step colloidal total synthesis, the key step is the photodeposition of a single AuNP tip onto either CdSe@CdS NRs or TPs. These AuNP tips then promote the deposition of a ferromagnetic cobalt shell to form dipolar Au@CoNPs, which act as the polymerizable unit in the colloidal polymerization via N−S dipole interactions (Figure 2). Hence, for the preparation of co- and terpolymers, AuNP tipping of CdSe NRs and TPs were conducted in separate steps, blended in solution and then subjected to CoNP deposition.

In the first step, CdSe@CdS NRs were prepared using the seeded growth approach of Pyun and co-workers, wherein wurtzite CdSe quantum dots (QDs) are initially prepared (D = 3.8 nm) and used to seed the growth of a CdS NR shell around the QDs.[16] For this study, NR lengths around 100 nm were targeted to enable facile discernment of composition via TEM in the resulting colloidal copolymers. Subsequently, these NRs were functionalized with a single AuNP tip using the photodeposition method of Banin et al., wherein the NRs are irradiated in the presence of an Au^{3+} precursor, amine reducing agent, and ammonium bromide surfactant to result in initial nonselective deposition of small AuNPs (<1 nm) onto various surfaces of the NR.[21] For this report, AuNP tipped CdSe@CdS NRs bearing a single large AuNP tip ($D \sim 7.5$ nm) were initially prepared. Furthermore, the addition of a slight excess of the AuNP reducing agent in this procedure allowed for both AuNP tipping onto CdSe@CdS NRs and the formation of free, bare AuNPs in solution. The ability to introduce free AuNPs into these reaction mixtures hence allows for introduction of "bare" Au@CoNP units into colloidal co- and terpolymers.

To synthesize the CdSe@CdS TPs bearing a single AuNP tip, a similar seeded growth motif was utilized as for NRs. Initially, highly uniform zinc blend (ZB) CdSe nanocubes ($D \sim$ 4.9 nm) were prepared as recently reported by our group,[18] which were then used to seed the growth of CdSe@CdS TPs with approximately 40 nm arms in high yield and without NR side products. These were then functionalized with a single AuNP ($D \sim 7.5$ nm) on the end of only one of the CdS arms via photodeposition in the same manner as for NRs, except

DOI: 10.1021/acsmacrolett.6b00511
ACS Macro Lett. 2016, 5, 950−954

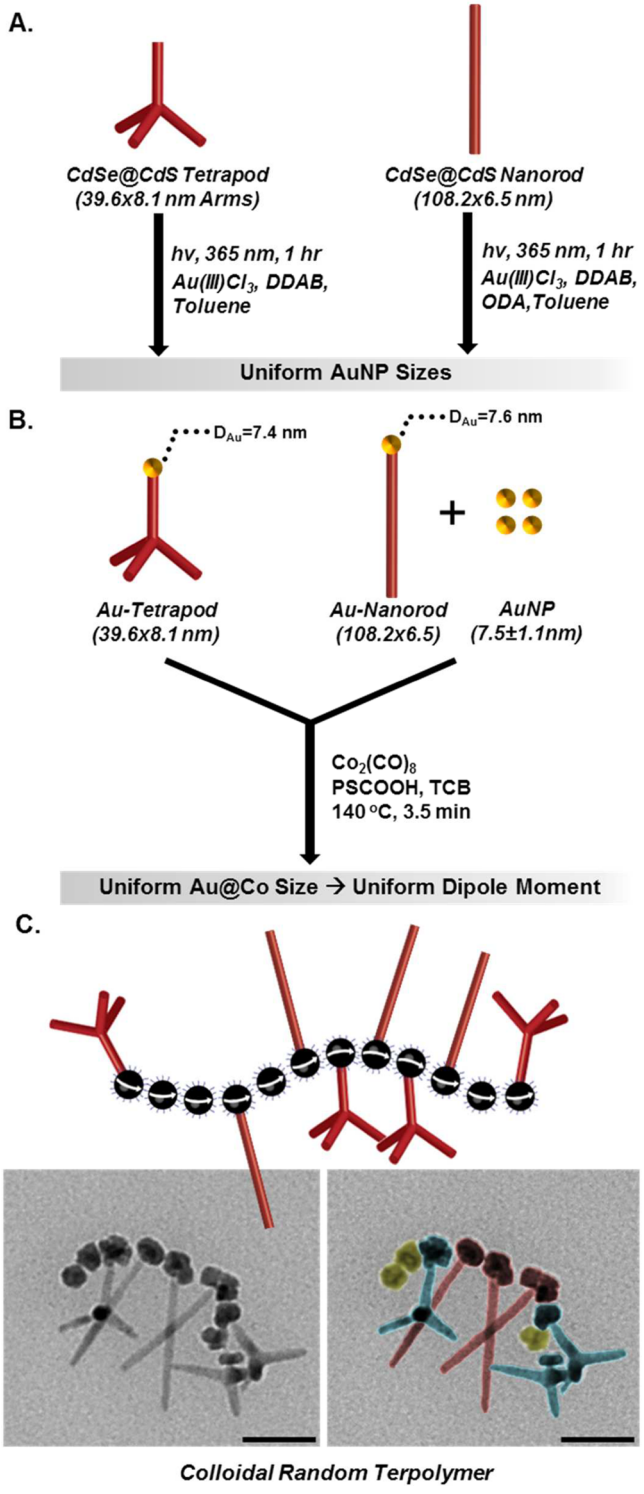


Figure 2. Total synthesis of colloidal random terpolymers. (a) Synthetic pathway to obtain Au-CdSe@CdS TPs. (b) Synthetic pathway to prepare Au-CdSe@CdS NRs. (c) Blending of AuTP and AuNR/AuNP comonomers and subsequent deposition of dipolar cobalt to result in colloidal polymers. A schematic representation of the terpolymer is shown (top), with a TEM image and processed image shown (right). All scale bars are 50 nm.

without the use of reducing agent, mitigating the formation of free AuNPs.

With these precursors in hand, the preparation of colloidal copolymers was then conducted by solution blending of these AuNP tipped CdSe@Cd NRs and TPs followed by overcoating of the AuNP tips with ferromagnetic CoNP shells. We found that it was most optimal to separately prepare CdSe@CdS NRs (L = 108.2 nm, W = 6.5 nm) and TPs (L_{arm} = 39.6 nm, W_{arm} = 8.11 nm) both with ∼7.5 nm AuNP tips, followed by solution blending into a single pot for the final CoNP deposition step which afforded CoNP tips of approximately 20 nm in size. For the deposition of dipolar CoNP shells onto AuNP-tipped semiconductor nanocrystals, the thermolysis of dicobaltoctacarbonyl ($Co_2(CO)_8$) was carried out at elevated temperature (140 °C) in 1,2,4-tricholorobenzene (TCB) using carboxylic acid terminated polystyrene ligands (PS-COOH; M_n = 8400 g/mol). TEM revealed that the CoNP tips on either CdSe@CdS NRs, or TPs were very similar in size ($D_{Co\ NR}$ = 19.8 ± 2.2 nm, $D_{Co\ TP}$ = 18.2 ± 2.7 nm), which further confirmed the role of AuNP tip size on semiconductor nanocrystal precursors.

TEM of both low and high coverage colloidal films enabled direct visualization of TP and NR side chains in colloidal copolymers, where the sequence and composition of these side chains were stochastic in nature, which confirmed that colloidal random copolymers were formed (for clarity, NRs are falsely colored-red and TPs are falsely colored-blue in Figure 2). Furthermore, the comparable incorporation of CdSe@CdS TPs and CdSe@CdS NRs into dipolar colloidal statistical copolymers indicated that the AuNP deposition step onto semiconductor nanocrystals directly influenced the size of the CoNP tip and the composition of the colloidal copolymer. *Hence, the control of Au and Au@CoNP tip size of these colloidal comonomers was analogous to the concept of modulating reactivity ratios of comonomer pairs in classical polymer science.* In this case, having CoNP tips (D ≈ 20 nm) on CdSe@CdS NRs (L = 108.2 nm) and CdSe@CdS TPs (L_{arm} = 39.6 nm) equated to equivalent reactivity ratios, allowing for the formation of colloidal random copolymers.

Due to the modularity of this approach, the composition of colloidal copolymers carrying NR or TP side chains was readily controlled by variation of molar feed ratios of AuNP tipped precursors. By reacting blends of AuNP tipped NRs and TPs with near identical tip sizes (7.6 ± 1.3 and 7.4 ± 1.3 nm, respectively), followed by deposition of dipolar cobalt, random copolymers composed of differing amounts of NRs and TPs could be prepared (Figure 3). In order to track colloidal copolymer composition as a function of monomer feed ratios, statistical analyses were performed on multiple separate electron microscope (EM) images of each of the polymers, for which the side chain for each of the individual cobalt nanoparticles present were individually identified (n = 500). In addition to qualitative assessment based on gross polymer morphology by EM, these analyses confirmed the tracking of colloidal polymer composition with AuNP tipped precursor ratios, with an excess of TPs (2:1 on a mole basis) in feed stocks resulting in TP enriched compositions of colloidal copolymers (1.6:1 by analysis) (Figure 3a). Conversely, variation of AuNP-tipped NRs (4:1 on a mole basis) in feed stocks were observed to enrich these units into colloidal copolymers materials (3:1 by analysis) (Figure 3b).

An attractive additional feature of this system is the ability to tune the size of dipolar CoNP tips and the resulting composition of colloidal copolymers (i.e., statistical vs segmented) by directly controlling the AuNP tip size on the semiconductor NR or TP (Figure 4). As we previously discussed, AuNP tipped CdSe@CdS NRs and CdSe@CdS TPs with very similar AuNP diameters (D = 7.6 ± 1.3 and 7.4

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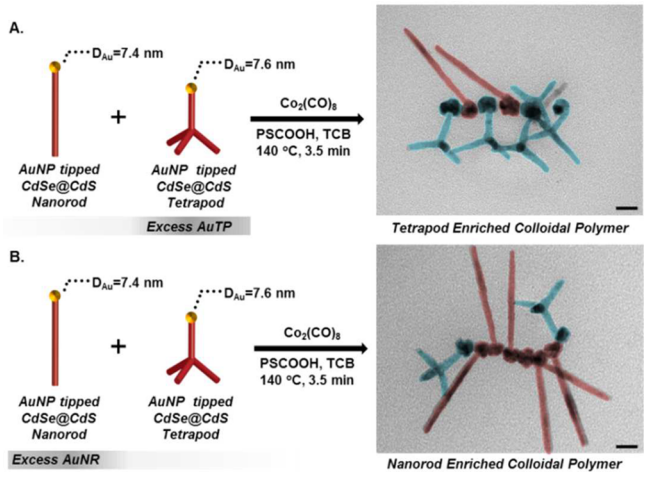

Figure 3. Control of random terpolymer composition by uniform Au-NP sizes and varied comonomer feed ratios. (a) Random copolymers formed with an excess of Au-CdSe@CdS TP colloidal monomers in the initial feed, resulting in excess TP-containing units in the polymer (1.6:1 TP/NR). (b) Random copolymers formed with an excess of Au-CdSe@CdS NR colloidal monomers in the initial feed, resulting in an excess of NR-containing units in the polymer (3:1 NR/TP). For each, a schematic representation of the polymer is shown, with a processed TEM image for clear monomer visualization. All scale bars are 20 nm.

± 1.3 nm, respectively) afforded CoNP tips of comparable sizes ($D \sim 20$ nm), which formed colloidal random copolymers (Figure 4a). However, the sizes of AuNP tips can be easily modulated during the photodeposition step, which we exploited to prepare CdSe@CdS NRs with a single very small AuNP tip ($D = 1.3 \pm 0.4$ nm) and CdSe@CdS TPs with a single larger AuNP tip ($D = 10.5 \pm 1.8$ nm). When these AuNP tipped semiconductor nanocrystals are solution blended in TCB (1:1 molar feed ratios) and then subjected to the previously described CoNP deposition reactions, we observe that CdSe@CdS NRs possessed small CoNP tips ($D = 11.5 \pm 2.0$ nm) relative to CoNP tips ($D = 22.2 \pm 2.6$ nm) on CdSe@CdS TPs, which directly correlate to the size of the AuNP seed. However, the differences in the sizes of these CoNP tips resulted in more selective magnetic associations which suppressed chain randomization and promoted the formation of colloidal block copolymers (Figure 4b). Due to the differences in CoNP tip size, this also resulted in different magnetic properties, where larger CoNP tips preferred to self-associate with other larger CoNP tips of comparable size and magnetization, followed by similar self-association tendencies with the smaller CoNP tips to form colloidal copolymer segments. These dipolar association tendencies can be attributed to more efficient neutralization of N−S NP dipoles with other N−S NP dipoles of equivalent size, magnetization, and magnetic flux. The direct association of a larger and smaller CoNP tip would be possible, but this less energetically favorable self-association of differently sized CoNPs would only occur after depletion of the preferred CoNP associations (see Supporting Information, Figure S11 for an example of segmented colloidal copolymers formed by blending of dipolar CoNPs of different sizes). Ultimately, these findings revealed that the composition of colloidal copolymers can be easily tuned from segmented vs statistical sequencing, which can be directly controlled by the size and reactivity of the AuNP tip. This for the first time, to our knowledge, points to the ability to tune the reactivity ratios of these colloidal copolymers, where AuNP tips of equivalent size ultimately affords statistical compositions, while AuNP tips of different sizes followed by CoNP overcoating enables the formation of colloidal block copolymers.

In conclusion, the synthesis of colloidal random copolymers and terpolymers composed of functionalized and bare dipolar Au@Co NPs has been achieved, and control over composition has been demonstrated. Additionally, for the first time it has been shown that the size of AuNPs prior to colloidal polymerization directly controls copolymer compositions, with comparably sized AuNPs resulting in random copolymers and highly differently sized tips resulting in segmented polymers. A consequence of CoNP size tracking with AuNP diameter, this finding provides a unique method to control colloidal monomer reactivity ratios and, thus, mesoscopic colloidal copolymer composition.

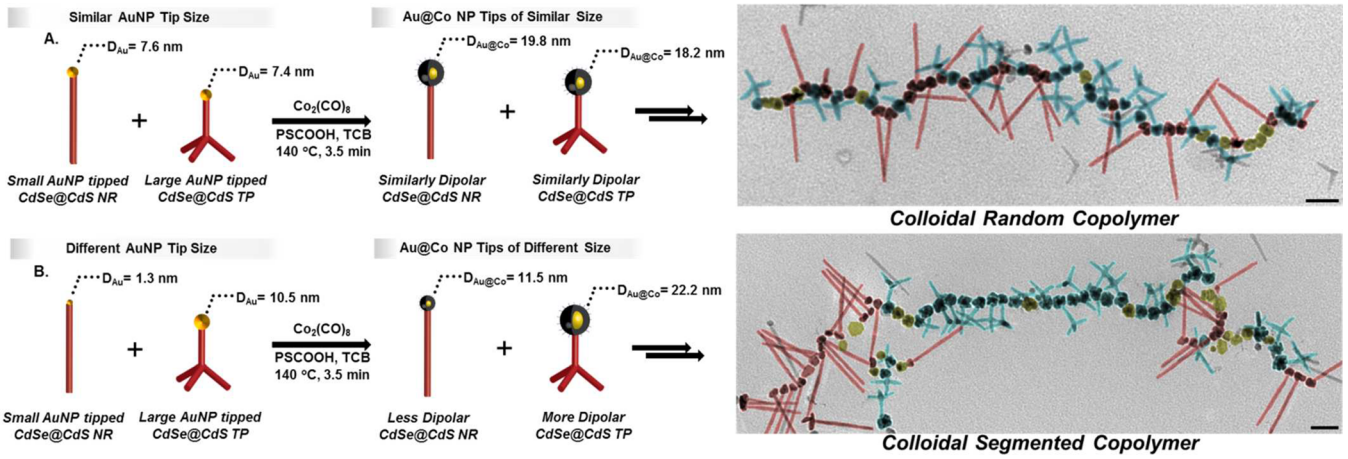

Figure 4. Effect of Au-NP tip size on colloidal polymer morphology with identical molar feed ratios. (a) Random copolymers formed from monomers with AuNP tips of near identical size and (b) Segmented copolymers formed from monomers with significantly differently sized tips. Processed, color coded TEM images are provided for NR (red) and TP (blue) side chain visualization. All scale bars are 50 nm.

DOI: 10.1021/acsmacrolett.6b00511
ACS Macro Lett. 2016, 5, 950−954

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00511.

Experimental details for the preparation and characterization of sulfur copolymers (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the NSF (DMR-1307192 for N.G.P., J.T.D., E.D.H., J.P.), Division of Chemical Science, Geosciences and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG03-02ER15753; N.G.P., J.P.), the Ventana/GIGA Summer Assistantship Award (for N.G.P.). K.C. acknowledges financial support from NRF through the National Creative Research Initiative Center for Intelligent Hybrids (2010-0018290).

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